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**Molecule-Sized Gates Based on Surface-Confined Dendrimers\*\***

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[\*\*] Interactions Between Organized, Surface-Confined Monolayers and Liquid-Phase Probe Molecules Part 5. We are grateful to the U. S. Office of Naval Research and the Robert A. Welch Foundation for support of this work. We also thank Dr. Antonio J. Ricco and Dr. Thomas M. Mayer (Sandia National Laboratories) for comments and suggestions. The authors also gratefully acknowledge Dendritech, Inc. (Midland, MI) for supplying samples of the Starburst™ PAMAM dendrimers used in this study.

In this report we demonstrate for the first time that surface-confined dendrimers<sup>[1-5]</sup> embedded within self-assembled monolayers (SAMs) of alkylthiols<sup>[6]</sup> can act as ion gates of molecular dimension.<sup>[7,8]</sup> These composite organic thin films are conceptually, structurally, and chemically very similar to the membrane/protein composites found in nature.<sup>[9]</sup> The key findings of this paper are that dendrimers can be well sealed within self-assembled alkylthiol monolayers and that as a function of the chemical state of the dendrimer, probe molecules can selectively and fully penetrate the dendrimer interior, exchange electrons within the dendrimer, and then diffuse back into the bulk solution. Molecular systems such as these are relevant for applications in electrocatalysis, chemical sensing, and separations.

Prior to the work described here, we showed that generation 0-8 (G0-G8) amine-terminated poly(amidoamine) (PAMAM) dendrimers<sup>[10]</sup> could be immobilized on surfaces by

covalent attachment of the dendrimer amine groups to the acid terminus of a mercaptoundecanoic acid SAM.<sup>[1,11]</sup> Here, we show that PAMAM dendrimers form high-density monolayers on Au surfaces, without the need for an intervening SAM adhesion layer, primarily as a consequence of multiple amine/Au interactions. This represents a major simplification of the previously described linking procedure. Additionally, we find evidence that single-component dendrimer monolayers result in a dendrimer conformation that is quite unlike the spherical form of G4 and higher generation PAMAM materials. On the surface, the G4 PAMAM dendrimers have a much larger footprint and are thinner than would be expected from their solution-phase diameter of 4.5 nm.<sup>[1,12]</sup> This is a consequence of the dendrimer's high degree of elasticity and strong interactions between the amine terminal groups and Au. In contrast, however, when a dendrimer monolayer is exposed to hexadecyl mercaptan ( $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ , C16SH), the thiol competes for Au sites and compresses the monolayer along its axis parallel to the surface. Thus, although little or no dendrimer is displaced from the surface, our data suggest that the dendrimer conformation changes to that of an on-end oblate spheroid as shown in Scheme 1. Finally, and most significantly, when two-component monolayers composed of a G4 PAMAM dendrimer and (C16SH) are co-adsorbed onto a Au electrode and then exposed to the redox probe molecules  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  at pH=6.3, we find that only the negatively charged  $\text{Fe}(\text{CN})_6^{3-}$  can penetrate the composite monolayer and undergo electron exchange with the underlying electrode. This is a consequence of the protonated terminal amine groups of the dendrimers. However, when the dendrimers are fully deprotonated at pH=11, both redox probe molecules undergo electron transfer. This effect is fully reversible as the pH is toggled between 6.3 and 11. Significantly, we provide unambiguous evidence for the first time that penetration of the redox probe molecules occurs *through* the interior of the dendrimers.<sup>[13-15]</sup>

Part a of Figure 1 shows an FTIR-external reflection spectrum (FTIR-ERS) of a G4 PAMAM monolayer prepared by immersion of a Au/Ti/Si(100) substrate in a 0.1 mM ethanolic solution of the dendrimer for 20 h, followed by careful rinsing and drying in flowing  $\text{N}_2$ . The

relevant peaks that confirm attachment of the dendrimer to the surface arise from the dendrimer framework: the amide I and amide II bands at 1661 and 1552  $\text{cm}^{-1}$ , respectively, and bands resulting from the two kinds of methylene groups present in PAMAM dendrimers at 2926, 2852, and 2818  $\text{cm}^{-1}$  [16] and the amide and amine N-H stretching modes centered around 3300  $\text{cm}^{-1}$ . surface acoustic wave (SAW)-based mass titrations<sup>[17]</sup> indicate that about 88±2% of the Au surface is occupied by the dendrimers after this step. Part b of Figure 1 shows the effect of immersing the dendrimer-modified electrode in a 1 mM ethanolic solution of C16SH for 20 h: there is a dramatic increase of the band intensity in the hydrocarbon region, confirming adsorption of C16SH to the Au surface, and a slight increase in the amide bands, which probably results from the orientational change induced in the dendrimer structure by the C16SH SAM (Scheme 1). The important point is that after exposure to C16SH, the dendrimer number density does not change significantly from its original value, but there is a shear force induced by the C16SH SAM that results in lateral compression of the dendrimers. On the basis of the mass titrations, FTIR-ERS, and ellipsometry<sup>[18]</sup> we estimate that the percentage of the surface accessible to the thiol increases from 12% to >50% after exposure to C16SH.

Figure 2 shows cyclic voltammetric data obtained from the mixed G4/C16SH monolayer corresponding to Figure 1b. At low pH (Figure 2a) the terminal amine groups of the dendrimers are protonated (p $K_a$  about 9.5)<sup>[12]</sup> and effectively block penetration, and hence electrochemical reduction, of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . In contrast, the rate of reduction of negatively charged  $\text{Fe}(\text{CN})_6^{3-}$  is only slightly hindered compared to that at a naked Au electrode. Contrast these results with those obtained at high pH (Figure 2b) when the amine groups are in their neutral form. In this case, both the  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  penetrate the dendrimer portion of the mixed SAM. This result alone, however, does not definitely prove intradendrimer mass transfer of the redox probes, since the observed effect could arise from probe penetration at the dendrimer/C16SH interface. Because of the strong shear force exerted on the dendrimers by C16SH, we view this as an unlikely scenario, but to definitively show that the dendrimers themselves, rather than

dendrimer-induced defects in the monolayer, are acting as molecular gates we performed two additional experiments.

In the first experiment, we prepared a G4 monolayer as described previously, converted the terminal amine groups to 4-(trifluoromethyl)benzamido groups, soaked the resulting dendrimer surface in C16SH, and then examined the electrochemical response in the presence of  $\text{Fe}(\text{CN})_6^{3-}$  at pH 6.3. Conversion of the surface-confined dendrimer to the fluorinated derivative (G4-F), without loss of dendrimer from the surface, is confirmed by the appearance of the new  $\text{CF}_3$  band in the FTIR-ERS spectrum at  $1329 \text{ cm}^{-1}$  and the slight increase in amide-band intensity resulting from coupling of the 4-(trifluoromethyl)benzoyl groups to the amine-terminated dendrimer (Figure 1c). Figure 3 compares the cyclic voltammetry that arises from G4 and G4-F: the protonated amines pass  $\text{Fe}(\text{CN})_6^{3-}$ , but the bulky and hydrophobic 4-(trifluoromethyl)benzamido groups prevent penetration. If penetration occurred primarily at defects in the G4/C16SH interface rather than through the dendrimer interior, then we might anticipate similar responses for the fluorinated and unfluorinated dendrimers.

A second experiment provides additional evidence for intradendrimer mass transfer of the redox probes. Figure 4 shows results for cyclic voltammetric experiments obtained using electrodes prepared from mixed monolayers composed of G0, G4, or G8 dendrimers and C16SH for both positively and negatively charged redox probes at pH=6.3. Considering first the results obtained using the  $\text{Fe}(\text{CN})_6^{3-}$  probe (Figure 4a), we observe that the Faradaic current decreases as a function of increasing dendrimer generation. This result is a consequence of steric crowding on the exterior of the dendrimer as the number of terminal groups increases and a corresponding reduction in permeability. A similar trend is observed for  $\text{Ru}(\text{NH}_3)_6^{3+}$  (Figure 4b), but the currents are much lower for all three dendrimer generations compared to that observed for  $\text{Fe}(\text{CN})_6^{3-}$ , because of the electrostatic repulsion of the probe by the positively charged dendrimer surface.

In summary, we have reported four new findings. First, PAMAM dendrimers adsorb irreversibly onto Au at high surface concentrations. Second, surface-confined dendrimers

undergo a dramatic conformational change upon exposure to C16SH resulting from shear compression. Third, and most significantly, the dendrimers act as molecular gates in that they can be tailored to permit selective intradendrimer mass transfer. Finally, we have shown that the primary amines of the surface-confined dendrimers can be easily functionalized without significant loss of dendrimer. These four key results open the door to a new generation of dendrimer-modified surfaces suitable for a range of technologically important applications.

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(18) Ellipsometric measurements indicate that a G4-modified surface changes in thickness from  $1.9 \pm 0.2$  to  $3.7 \pm 0.1$  nm after exposure to an ethanolic C16SH solution. Ellipsometric modeling results derived from the Bruggemann effective-medium approximation data suggest a change in the calculated, single-dendrimer height from 2.8 to 5.5 nm. (H. Tompkins *A Users Guide to Ellipsometry*; Academic: New York, 1993; Appendix B.) Previously reported theoretical calculations (see ref. 10) are consistent with this result.

**Key Words:** Dendrimer, Modified Electrode, Electrochemistry, Supramolecular

#### Figure Captions

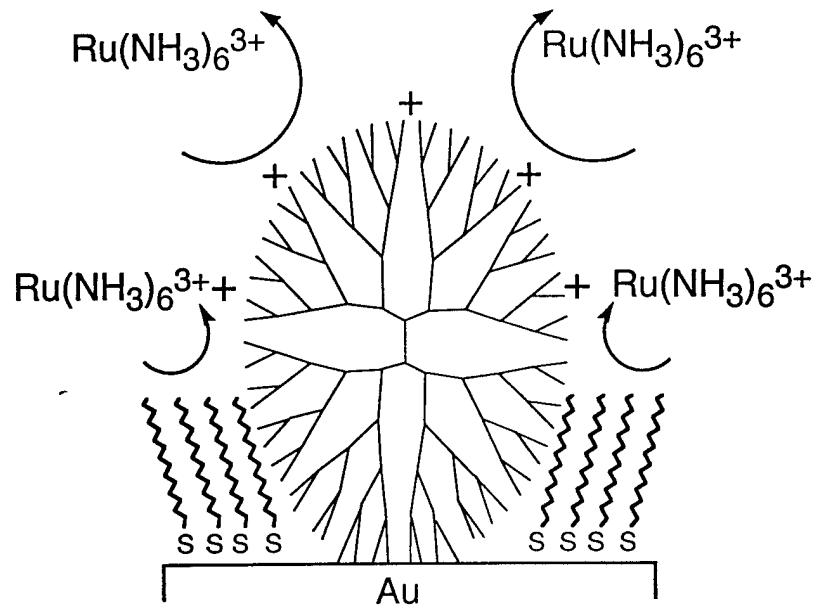
**Figure 1.** FTIR-ERS spectra of G4 dendrimer-modified Au substrates. (a) G4 only; (b) G4 after immersion in an ethanolic solution of C16SH; (c) G4 followed by on-surface conversion of the primary amine groups to 4-(trifluoromethyl)benzamido groups and subsequent immersion in an ethanolic solution of C16SH.

**Figure 2.** Cyclic voltammetry of 5 mM  $\text{Fe}(\text{CN})_6^{3-}$  and 5 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  in 0.5 M aqueous  $\text{Na}_2\text{SO}_4$  electrolyte solutions at G4/C16SH-modified Au electrodes: (a) pH=6.3 (0.025 M  $\text{Na}_2\text{HPO}_4$  + 0.025 M  $\text{NaH}_2\text{PO}_4$ ), and (b) pH=11 (0.036M  $\text{NH}_4\text{Cl}$  + 2.0 M  $\text{NH}_4\text{OH}$ ). Electrode area: 0.086  $\text{cm}^2$ , scan rate: 50 mV/s.

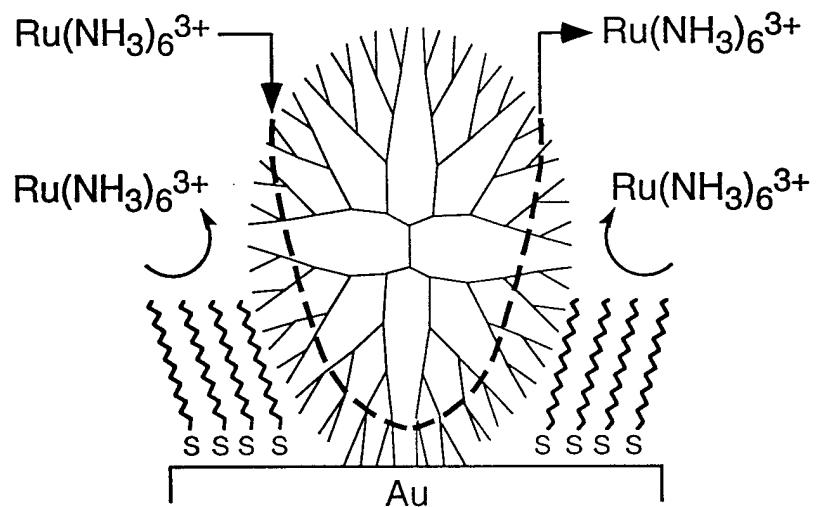
**Figure 3.** Cyclic voltammetry of 5 mM  $\text{Fe}(\text{CN})_6^{3-}$  at a (a) G4/C16SH-modified Au electrode, and (b) a G4-F/C16SH-modified electrode in a 0.5 M aqueous  $\text{Na}_2\text{SO}_4$ , pH=6.3 (0.025 M  $\text{Na}_2\text{HPO}_4$  + 0.025 M  $\text{NaH}_2\text{PO}_4$ ) electrolyte solution. Electrode area: 0.086  $\text{cm}^2$ , scan rate: 50 mV/s.

**Figure 4.** Cyclic voltammetry of 5 mM solutions of (a)  $\text{Fe}(\text{CN})_6^{3-}$  and (b)  $\text{Ru}(\text{NH}_3)_6^{3+}$  at G0/C16SH-, G4/C16SH-, and G8/C16SH-modified Au electrodes in a 0.5 M aqueous  $\text{Na}_2\text{SO}_4$ , pH=6.3 (0.025 M  $\text{Na}_2\text{HPO}_4$  + 0.025 M  $\text{NaH}_2\text{PO}_4$ ) electrolyte solution. Electrode area: 0.086  $\text{cm}^2$ , scan rate: 50 mV/s.

pH = 6.3



pH = 11.0



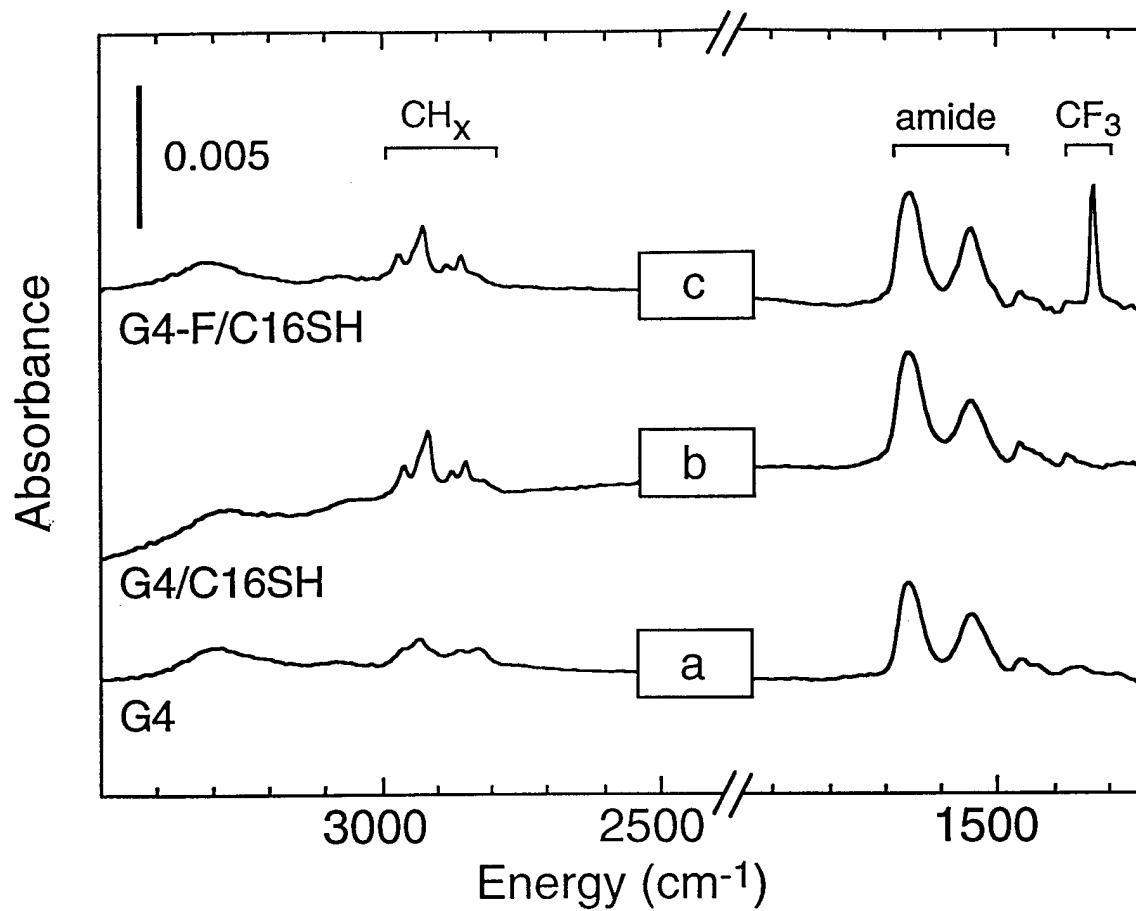


Figure 1 / Zhao et al.

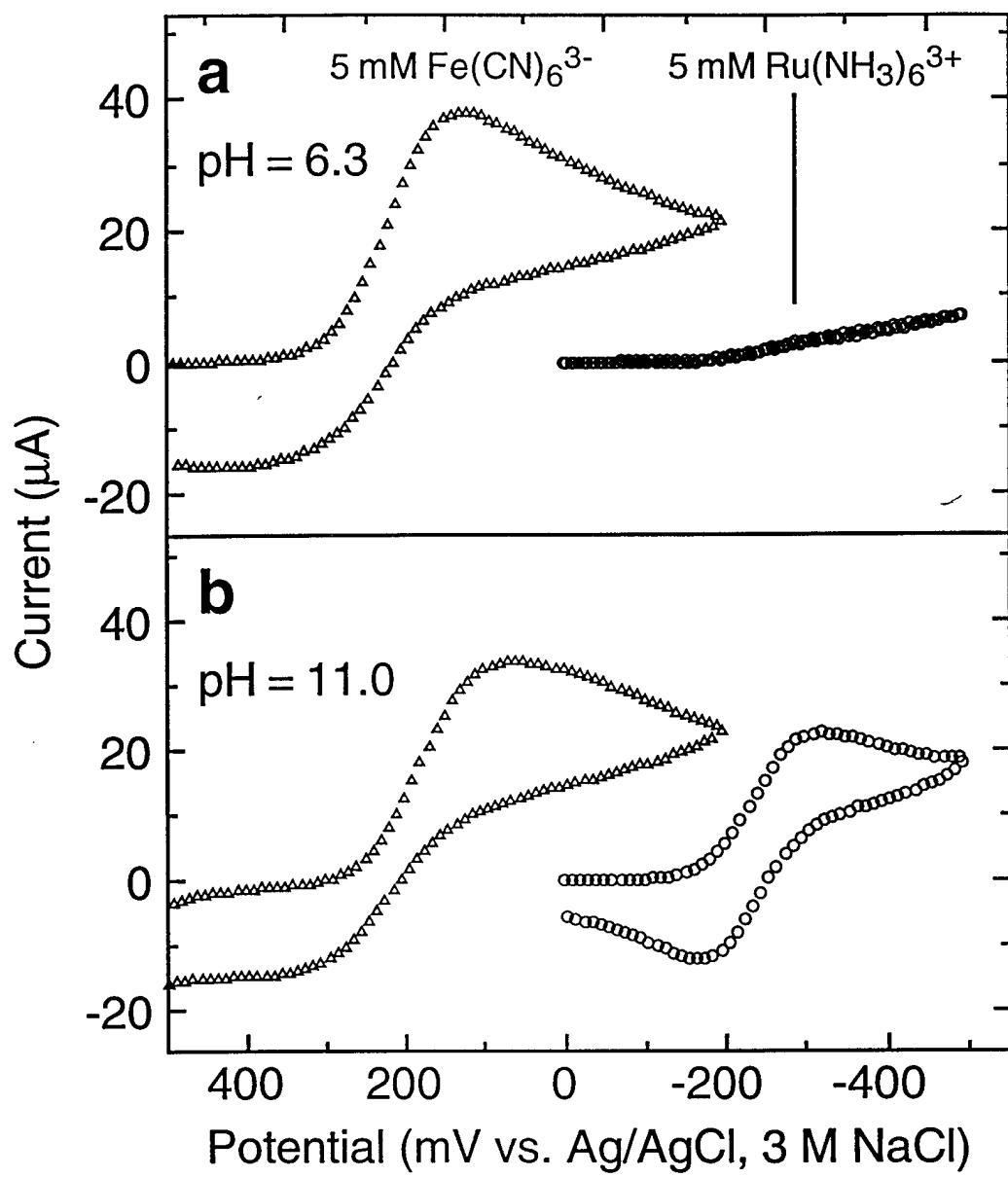


Figure 2/Zhao et. al

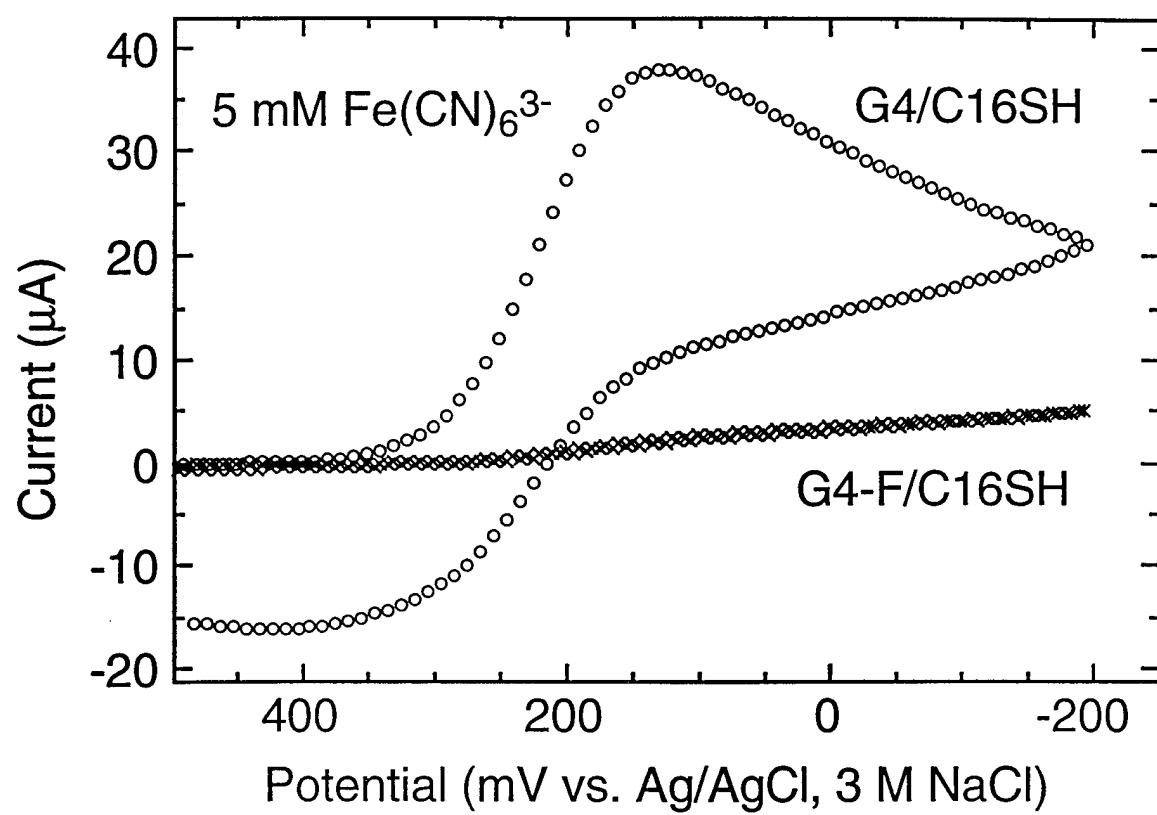


Figure 3/Zhao et. al

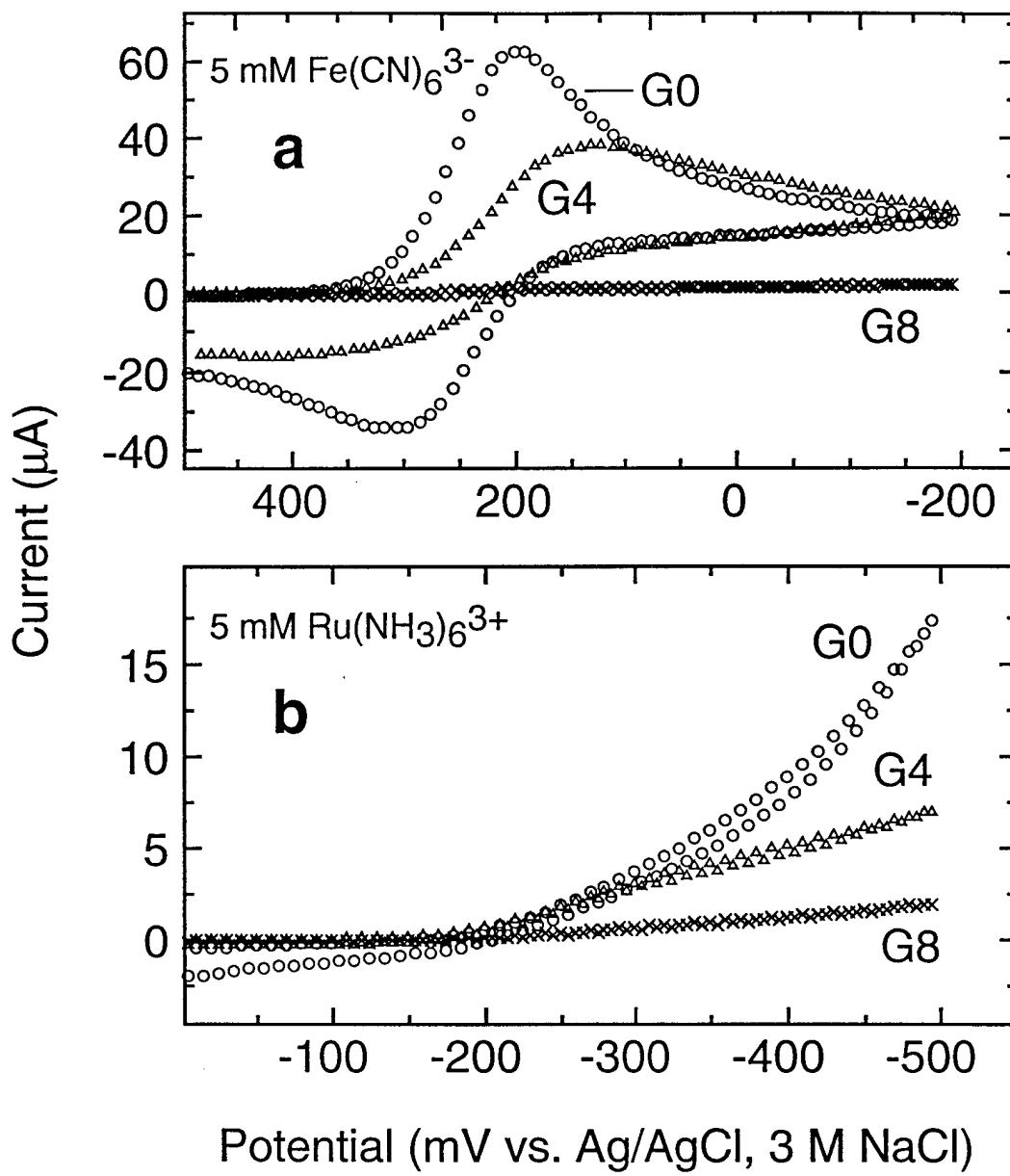


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